

**10/589592****IAP11 Rec'd PCT/PTO 15 AUG 2006**  
- 1 -**PROCESS AND PLANT FOR ELECTRODEPOSITING COPPER****Technical Field**

- 5      The present invention relates to a process for the electrochemical winning or refining of copper by electrodepositing copper from an electrolyte solution containing the metal in ionogenic form, in which the electrolyte is passed through an electrolysis plant comprising at least one electrolytic cell, which in an electrolyte tank for receiving the electrolyte has at least two electrodes serving as anode and cathode, which are alternately arranged at a distance from each other, and to a corresponding plant.
- 10

For producing copper, a multitude of processes are known, in particular pyrometallurgical and hydrometallurgical processes. In pyrometallurgical processes, enriched chalcopyrite is molten in a suspension furnace or bath-type melting furnace by adding oxygen to obtain a copper matrix, in converters is then converted to crude copper in two blowing steps, and is purified further in a final electrolytic refining step. This electrolysis is also referred to as refining electrolysis. In hydrometallurgical processes, on the other hand, in particular low-copper oxidic ores with a copper content of about 0.5 to 1 wt-% are used as starting materials. The starting ore poor in copper, which due to its mineralogical composition cannot always be processed economically with other processes such as flotation, is leached e.g. with dilute sulfuric acid, and in an extraction plant the resulting solution rich in copper is treated with an organic extractant which selectively extracts copper ions from the solution. Subsequently, the copper-containing extractant is stripped with foul electrolyte with a copper content of about 30 to 40 g/l, which originates from the succeeding electrolysis plant, the copper from the extractant phase passing over into the electrolyte, which upon further purification for removing extractant residues and solids typically is recirculated to the electrolysis plant with a copper content of 40 to 50 g/l. Such electrolysis is also referred to as extraction electrolysis.

15

20

25

30

During operation of the electrolyses, the copper ions are reduced at the cathodes and deposited as elementary copper. Conventional electrolysis plants for the electrometallurgical winning of copper, as they are described for instance in J.A. Wells and W.R.

Snelgrove, The Design and Engineering of Copper Electrowinning Tankhouses, Proceedings of the International Symposium on Electrometallurgical Plant Practise, Pergamon Press, 1990, pp. 57 to 72, comprise up to 188 electrolytic cells, each of which has between 20 and 60 cathodes, chiefly made of stainless steel, as well as a corresponding number of anodes. At predetermined distances, depending on the size of the plant, the copper-coated cathodes are withdrawn from the electrolytic cell manually or by means of cranes and transferred to a stripping plant, in which the copper coatings are peeled (stripped) off the cathodes, before the cathode starting sheets are returned to the electrolytic cells after a corresponding aftertreatment. The copper peeled off is finally processed in melting furnaces.

For an efficient aftertreatment of the copper-loaded cathodes, in particular for peeling off the deposited copper in the stripping machine, a rather uniform deposition of the copper on the cathodes, based on the surface area of the cathodes, is desirable. This is only ensured with a uniform streamline distribution along the length of the cathodes. As is described for instance in A. Schmidt, Angewandte Elektrochemie, Verlag Chemie 1976, pp. 49 to 51, the uniformity of the streamline distribution with a given conductivity of the electrolyte is, however, increasing with decreasing width and in particular length of the electrode surface immersed into the electrolyte. In addition, the streamline distribution depends on the conductivity of the electrode material and on the current density applied during electrolysis. Due to these relations, both the refining electrolysis and the extraction electrolysis typically employ electrodes with a surface area maximally immersed into the electrolyte of about 1x1 meter. The melting furnaces for the further processing of copper are also adjusted to this size.

Due to the high investment and operating costs of the electrolysis plants and cathode processing plants comprising crane and stripping machines, which are combined in the so-called tankhouse, attempts have been made for quite some time at increasing the economic efficiency of both the refining electrolysis and the extraction electrolysis. This largely depends on the efficiency of the electrolysis as well as on the number of the cathode movements and therefore on the amount of copper deposited per cathode.

To increase the efficiency of the electrolysis, it is desirable to increase the current density during the electrolysis, in order to achieve a higher deposition of copper on the cathodes per unit time. However, the current density on the cathode side is limited by the quality of the copper deposited, as due to the increased overvoltage on the cathodes more impurities are deposited with increasing current density. On the anode side, the lead alloy used as electrode material for the extraction electrolysis becomes more unstable, and the copper anode used for the refining electrolysis becomes passivated with increasing current density. As a result of these two effects, present-day electrolyses operate with a maximum current density of about  $370 \text{ A/m}^2$  electrode surface. In the extraction electrolysis, a higher current density can only be achieved by using expensive anode materials with a lower quality of the electrodeposited copper.

Therefore, a further reduction of the production costs with a consistent quality of the electrodeposited copper can only be achieved by reducing the specific investment and operating costs of the cathode processing plants comprising the crane and stripping machines, i.e. by decreasing the necessary number of cathode movements based on the amount of copper electrodeposited per cathode.

#### Description of the Invention

It is the object of the present invention to increase the copper loading per cathode based on the number of cathode movements with a consistent quality of the electrodeposited copper.

In accordance with the invention, this object is solved by a process and a plant with the features of claims 1 and 23, respectively. Preferred embodiments of the invention are evident from the dependent claims.

Surprisingly, it could be found in accordance with the present invention that – contrary to the prejudice existing among experts that electrodes with an electrolyte immersion surface of more than  $1 \times 1 \text{ m}$ , and in particular electrodes with an electrolyte immersion depth of more than 1 m, are not suitable for winning copper due to the non-uniform streamline distribution necessarily obtained at the electrodes – an electrolyte immer-

sion depth of the electrodes of more than 1.2 m leads to a sufficiently uniform deposition of copper on the cathodes in processes for electrodepositing copper from an electrolyte solution containing the metal in ionogenic form also with the cathode materials commonly employed in the refining and extraction electrolyses and with the usually  
5 adjusted current densities. Here as well, an efficient processing of the loaded cathodes, in particular a stripping of the copper deposited, is possible with the known processing techniques. In the process of the invention, more copper is produced per cathode movement than in known processes with a consistent quality of the electrodeposited copper due to the greater electrolyte immersion depth, so that the costs per ton of  
10 extracted copper can be decreased drastically.

During operation of the electrolysis, the immersion depth of the electrodes into the electrolyte preferably is an integral multiple of the commonly used immersion depth of about 1 m and particularly preferably about 2 m with a cathode width of about 1 m  
15 each. The advantage is that the melting furnaces, which because of the active cathode surface, i.e. the cathode surface immersed into the electrolyte, normally were designed for a size of 1x1 m in the known processes, can be used unchanged, in that the stripped copper sheets to be obtained with the process in accordance with the invention are reduced to the corresponding size of 1x1 m subsequent to the stripping operation  
20 and before being supplied to the melting furnace. With an active electrode length of 2 m, this can easily be achieved in that for instance the copper sheets are bent in the middle and are folded at the bending surface. It is likewise possible to obtain two separate cathode sheets each of 1x1 m during the stripping operation, e.g. by an insulated horizontally circumferential region provided at about the level of half the cathode height,  
25 so that another folding or reduction in size is made superfluous. Finally, a mechanical separation is also possible.

In accordance with a development of the invention it is proposed that the at least one electrolytic cell has more than 60 cathodes, particularly preferably more than 100 cathodes, and quite particularly preferably 114 cathodes. As a result, the efficiency of the process of the invention is further increased, as the size of the electrolytic cells caused by this measure provides for an inexpensive transport while at the same time reducing the number of cells per production capacity. This leads to a smaller tank-

house, shorter cathode delivery paths and less stray currents. In principle, the cathodes can be made of all materials known to the skilled person for this purpose, stainless steel cathodes being preferred.

5 It turned out to be advantageous to perform the electrolysis with a current density as used in the known processes, preferably with a current density of more than  $200 \text{ A/m}^2$ , and particularly preferably with a current density between  $250$  and  $370 \text{ A/m}^2$ . In this way, the deposition of major amounts of impurities on the cathodes is avoided and copper is produced with the required quality. Due to the greater active electrode length  
10 and surface area, higher specific current intensities, i.e. higher current intensities per electrode, are obtained in the process of the invention as compared to the processes of the prior art. Whereas in the last-mentioned processes with cathodes and anodes of an active electrode surface of  $1 \times 1 \text{ m}$  each, the specific current intensity is  $740 \text{ A}$  per electrode with a current density of  $370 \text{ A/m}^2$ , the specific current intensity is doubled in  
15 accordance with the invention to  $1,480 \text{ A}$  per electrode when using electrodes with an active surface of  $1 \times 2 \text{ m}$ .

In the process of the invention, the electrodes can in principle be positioned in the electrolytic cells, be fixed and supplied with current in any way known to those skilled in  
20 the art. However, electrodes with a horizontal hanger bar known per se, which has a first end and a second end and preferably is made of the same material as the cathode surface, in particular steel, turned out to be advantageous. For power supply, one end of the hanger bar of the cathodes each rests on a first contact bar connected to a power source, whereas one end each of the hanger bar of the anodes each is in contact with a second contact bar connected to the power source. Preferably, the two contact bars are arranged on one contact bar each, which are provided at the edge of  
25 the electrolyte tank. The respectively second ends of the hanger bars of the electrodes can rest on a supporting surface of insulating material, which for instance is likewise arranged on the contact bars.

30 In accordance with a particular embodiment of the present invention, the electrodes have the first end of their hanger bar each resting on one of the two contact bars via a two-line contact. This is advantageous in particular because due to the larger specific

current densities in the process of the invention higher currents must be transmitted from the contact bars to the electrodes, which can be realized more effectively with two-line contacts due to the greater contact surface. For this purpose, a contact bar with an at least substantially trapezoidal indentation is used particularly preferably, onto 5 which the first end of the hanger bar is applied with a contact surface having an at least substantially rectangular cross-section. The two-line contact can of course also be effected in any other way known to the skilled person for this purpose.

To ensure a transmission of current rather free of losses between the contact bars and 10 the cathodes, which are for instance made of stainless steel, also with high specific current intensities, the process of the invention preferably employs cathodes whose e.g. steel-sheathed hanger bar has a copper core. Due to the high electric conductivity 15 of copper, the current thus transmitted from the contact bar to the hanger bar is transmitted to the active electrode surface with only minimal losses, whereas the steel sheath surface of the hanger bar provides the hanger bar in particular with a high mechanical strength and high corrosion resistance. Based on its cross-section, the copper core preferably has the same geometry as the hanger bar. In this case, a hanger bar made of steel, which for instance is substantially square in cross-section, likewise includes a substantially square copper core.

20  
...  
In accordance with a development of the invention it is proposed to have the respectively second end of the hanger bar of the cathodes rest on an equalizer bar preferably arranged on one of the two contact bars, irrespective of whether the contact of the other hanger bar ends with the contact bars is effected via a one-line or two-line contact or any other contact whatsoever. The advantage of this embodiment consists in 25 that the cathodes in this way have two electric contacts, namely on the one hand with a contact bar and on the other hand with an equalizer bar, whereby the distribution of current between the electrodes is rendered more uniform. This is expedient in particular with high specific current intensities, in order to minimize the transfer resistances and 30 electric losses.

For the same reasons, it is preferred in the process of the invention to also have the second end of the hanger bar of the anodes rest on an anode equalizer bar separate from the cathode equalizer bar.

- 5      In accordance with a particular embodiment of the present invention, the contact bars and/or possibly the equalizer bar or, particularly preferably, the intermediate contact bars, on which the contact bars and possibly the equalizer bars are arranged, are cooled during the electrolysis, in order to avoid a power loss, which results from the higher specific current intensity and the related higher current load, and a heating of the corresponding conductor bars. For this purpose, a water cooling of the conductor bars turned out to be particularly expedient, which is realized for instance by passing cooling water through a cooling water channel provided in the bus bars. Good results are achieved in particular with cooling water channels having a diameter of about 15 to 20 mm. Extruded bus bars with embedded cooling channel are preferably used for this purpose, although good results are also achieved with bus bars with milled slots, which are subsequently covered and welded, or with soldered copper tubes. For supplying water to the corresponding bus bars, tubes of PVC or hoses of vinyl material turned out to be particularly useful.
- 10     To achieve an efficient heat exchange between the bus bars and the cooling water, it is proposed in accordance with the invention to pass the cooling water through the cooling water channels with a velocity sufficient to maintain a turbulent water flow, where a velocity of about 1.5 m/s should, however, not be exceeded.
- 15     In accordance with the invention, the cooling water supply can also be effected by two coolant circuits divided into a primary circuit, which at least partly extends through the intermediate bus bars to be cooled, and a secondary circuit, which preferably extends completely outside the bus bars to be cooled. The connection of the two circuits can be effected in any way known to the skilled person. In particular, shell-and-tube heat exchangers as well as plate-type heat exchangers turned out to be useful. Particularly preferably, the primary circuit exclusively extends through the bus bars to be cooled and is operated with high-purity cooling water, for instance water purified by a reverse
- 20
- 25
- 30

osmosis plant, whereas the secondary circuit is fed with crude water and is recooled for instance by an atmospheric cooling tower.

To ensure that the primary circuit is always filled with cooling water, the same prefer-

5       ably includes a water expansion tank.

In accordance with a development of the invention it is proposed to provide a fluid distributor in the at least one electrolytic cell, through which during operation of the extraction electrolysis a liquid, a gas, a gas mixture or a mixture of gas and liquid is introduced, particularly preferably from below, into the electrolytic cell. Due to the convection flow generated by such introduction of fluid a better intermixing of the electrolyte is achieved, which is why the copper is deposited on the cathodes more uniformly. Furthermore, the convection flow effects a reduction in thickness of the boundary layers at the electrodes, which results in a better and faster mass transfer of the copper ions to the electrode surface. An introduction of fluid from below into the electrolytic cell is particularly preferred, because in the upper region of the cell a certain convection flow is obtained automatically due to the gas bubbles released at the anode during the extraction electrolysis, and therefore in particular in the lower region of the electrolytic cell an additional convection flow is important.

10

Preferably, electrolyte solution or a mixture of electrolyte solution and gas bubbles is introduced into the electrolytic cell through the fluid distributor. Since electrolyte continuously refreshed with copper sulfate from the leaching plant must in any case be supplied to the electrolytic cell during operation of the electrolysis, the fluid supply

15

system requires no increase in the investment and operating costs in the first case and only an insignificant increase thereof in the second case. To increase the convection, other liquids, gases or gas mixtures can also be supplied to the electrolytic cell instead of electrolyte solution or a mixture of electrolyte solution and gas bubbles, or other systems such as mechanical mixing devices or the application of ultrasound can be used.

20  
25  
30  
In accordance with a particular embodiment of the present invention, the fluid distributor, as it is of simple construction and efficient in terms of operating costs, consists of

two tubes arranged substantially parallel to the longitudinal sides of the electrolytic cells, which at their surfaces each have one or more fluid outlet holes. The tubes are disposed at a small distance from the side wall. The distance is defined by the fastening mechanism of the tube at the cell wall and provides for the deposition of electrolyte sludge at the cell bottom. Typically, the distance is 10-50 mm. The distance of the two tubes from the cell bottom should be chosen such that electrolyte sludge can be collected below the fluid distributor at the cell bottom. Typically, the distance from the cell bottom is 100-200 mm. As fluid supply conduit to the fluid distributor, there can for instance be used a tube arranged in the middle of the end face of the electrolytic cell, which with respect to the electrolytic cell extends vertically from the top to the bottom and at its lower end branches into two tubes extending horizontally and parallel to the end face of the electrolytic cell, one of which tubes is each connected with one end of the tubes of the fluid distributor, which extend substantially parallel to the longitudinal sides of the electrolytic cells.

15

To achieve an effective convection flow, the fluid distributor should have a high enough number of fluid outlet holes. In accordance with the present invention it was found that for this purpose the relative number of the fluid outlet holes with respect to the total number of electrode pairs per electrolytic cell is decisive. Preferably, the fluid distributor has 1-5, particularly preferably about 1-2 fluid outlet holes per electrode pair and cell side provided in the electrolytic cell.

20

The shape of the fluid outlet holes is less decisive in terms of the convection flow. However, it turned out to be advantageous to provide substantially circular fluid outlet holes.

25

However, what influences the quality of the convection flow achieved much more is the cross-sectional area of the fluid outlet holes. In the case of circular fluid outlet holes, the diameter thereof preferably is 1 to 10 mm, particularly preferably 5 to 7 mm, and in particular about 6 mm.

In accordance with a development of the invention it is proposed to provide at least two electrolyte outlets per electrolytic cell, in order to achieve a trouble-free overflow and promote a uniform distribution of the electrolyte in the electrolytic cell.

- 5      In accordance with a particular embodiment of the present invention, the cathodes used have an indentation of V-shaped cross-section at their lower longitudinal edge. Thereby, a densification of streamlines necessarily occurring at straight edges, which leads to an – undesired – increased deposition of copper at the edges, can be reduced and optimally even be prevented completely. During stripping, the indentation furthermore effects a separation of the front and rear sides deposited on the cathode into two cathode sheets.
- 10

The invention will subsequently be explained in detail with reference to embodiments and the drawing. All features, per se or in any combination, constitute the subject-matter of the invention, independent of their inclusion in the claims or their back-reference.

15

#### Brief Description of the Drawings

- 20     Fig. 1     shows the basic structure of an electrolysis plant for winning or refining copper;
- Fig. 2     shows a section along line A-A in Fig. 1;
- 25     Fig. 3     schematically shows a section through an electrolytic cell with a cathode held by a hanger bar;
- Fig. 4     schematically shows a section through an electrolytic cell with an anode held by a hanger bar;
- 30     Fig. 5     schematically shows two-line contacts between the hanger bar and a contact bar;

Fig. 6 schematically shows one-line contacts between the hanger bar and a contact bar with equalizer bar; and

5 Fig. 7 schematically shows the structure of a pilot plant for performing the process of the invention.

#### Description of the Preferred Embodiments

In the electrolysis plant for winning or refining of copper, which is schematically illustrated in Figs. 1 and 2, electrolytic cells 1 (dimensions L x W x H e.g. about 12.5 x 2 x 10 2.7 m) each with a plurality of e.g. 115 anodes 2 and 114 cathodes 3, which are each arranged alternately and are held at the edges of the electrolytic cells 1 via hanger bars 4, are provided in numerous cell rows.

15 Via a crane 5, the hanger bar 4 with the electrodes suspended thereon can be transported between a maintenance area 6 for the anodes 2, the cells 1 as well as a stripping machine 7, in which the copper deposited at the cathodes 3 is stripped in a manner known per se.

20 Fig. 3 schematically shows a cathode 3 resting on the edges of the electrolytic cell via the hanger bar 4. Correspondingly, Fig. 4 shows an anode 2 which is likewise held by a hanger bar 4. The anode 2 additionally has holes 8 for spacers, which ensure the required uniform distance between anodes and cathodes of e.g. 50 mm each.

25 Via a two-line contact 9, the one end of the hanger bars 4 rests on a contact bar 10 arranged at the edge of the electrolyte cell(cf. Fig. 5), which is connected with a non-illustrated power source via a bus bar. The other end of the hanger bar 4 rests on an equalizer bar 11. In general, this is effected via a one-line contact (cf. Fig. 6).

30 With the process in accordance with the invention, which is characterized by a high specific current intensity – based on the electrodes – more copper is produced than in the known processes due to the greater electrolyte immersion depth of the cathodes per cathode movement with a consistent copper quality. A cathode with an active

immersion surface increased to 2x1 m needs only to be withdrawn from the electrolyte tank for processing after a copper loading of 200 kg, whereas a conventional prior art cathode of 1x1 m must already be processed after a deposition of 100 kg copper. Thus, the effort involved in the cathode movements is halved by a factor of 2, so that, based  
5 on the same amount of copper produced, correspondingly smaller or less crane systems are required, for instance one instead of two cranes for handling the electrodes, a smaller number of stripping machines and thus less production area and personnel.  
The ground area required for mounting the electrolytic cells in the tankhouse is also drastically reduced. In the process in accordance with the invention, on the other hand,  
10 different contact bars and possibly equalizer bars are required due to the higher specific current intensity, and for the subsequent processing of the loaded cathodes crane systems with a higher load-bearing capacity are required due to the higher weight of these cathodes. The height of the tankhouse between upper cell edge and crane path must be adjusted for processing the extended cathodes, and the same is true for  
15 mounting the electrolytic cells with increased overall height. Due to the greater cathode surface, differently sized stripping machines as well as folding or comminution machines for folding the larger copper sheets before supplying the same to a melting furnace designed for conventional plants are required. As both investment and operating costs for the last-mentioned measures are smaller than the corresponding savings  
20 achieved due to the smaller number of cathode movements, a significant decrease of the production costs is achieved on the whole.

Based on an annual production of 120,000 tons, a comparison of the process of the invention, which is performed with an active electrode surface of 2x1 m, with the prior art process performed with an active electrode surface of 1x1 m, but twice the number  
25 of electrodes with the same current density, yields the following characteristics:

	Prior art process	Inventive process
Amount of copper per m <sup>2</sup> cell area (in t)	40	65
Amount of copper per m <sup>2</sup> tankhouse (in t)	20	30
Amount of copper per m <sup>3</sup> tankhouse (in t)	1.9	2.3
Cathode movements per day	3120	1560

When using the process of the invention, the investment costs for corresponding plants for the electrochemical extraction of copper thus can be decreased by up to 20%, and the production costs can be decreased by up to 10%.

## 5 Example

In the test stand for performing verification tests on a pilot scale as shown in Fig. 7, two electrolytic cells 1a, 1b connected in parallel with respect to the electrolyte supply and a common electrolyte preparation and circulation system are provided. Both electrolytic cells are electrically connected in series (not shown). The electrolytic cell 1a is equipped with two lead anodes (A, width of 0.5 m and height of 2 m, immersed surface) and a centrally arranged cathode K. The electrolytic cell 1b has 3 anodes (A, width of 0.5 m and height of 1 m, immersed surface) and two cathodes K of equal size. The used number and size of the electrodes leads to the fact that in the case of a series connection equal current densities are achieved in both electrolytic cells.

Both electrolytic cells are charged with the same amount of fresh electrolyte (20a and 20b). The inflow of electrolyte is adjusted such that during a stationary operation of both electrolytic cells a copper depletion of about 1.5 g/l is obtained. The depleted solution 21a and 21b, respectively, is supplied to the electrolyte circuit. It comprises a stirred leaching tank 22, in which the depleted amount of copper is compensated by adding copper oxide 23. The overflow of the leaching tank 22 (enriched electrolyte 25) is introduced into a pump recipient tank 24. The pump recipient tank 24 is electrically heated by the heater 26 and stirred by partial recirculation of the enriched electrolyte 25'. The pump 27 is used for circulating the electrolyte.

In pilot tests, a synthetically produced sulfuric-acid copper sulfate solution was used as electrolyte. To improve the cathode morphology, a small amount of guar solution (not shown) was added to the pump recipient tank 24. The current density used was 300 A/m<sup>2</sup>. Several tests were performed, which took 5 to 7 days. In all tests, cathodes of very good quality were produced in both cells. The copper quality achieved was independent of the cathode size. In all tests, a current efficiency > 90% was achieved (Table 1, all concentrations at the cell inlet, e.g. cell 1a):

Test	Cu Content (g/l)	H <sub>2</sub> SO <sub>4</sub> (g/l)	Current density (A/m <sup>2</sup> )	Test period (h)	Voltage (V)	Current efficiency (%)
1	45	120	300	161	2.1	95
2	47	140	300	167	2.05	91
3	55	135	300	189	2.1	94

**List of Reference Numerals**

- |    |                             |
|----|-----------------------------|
| 1  | electrolytic cell           |
| 2  | anode                       |
| 5  | 3      cathode              |
|    | 4      hanger bar           |
|    | 5      crane                |
|    | 6      maintenance area     |
|    | 7      stripping machine    |
| 10 | 8      holes                |
|    | 9      two-line contact     |
|    | 10     contact rail         |
|    | 11     equalizer bar        |
|    | 20a,b fresh electrolyte     |
| 15 | 21a,b depleted solution     |
|    | 22     leaching tank        |
|    | 23     copper oxide         |
|    | 24     pump recipient tank  |
|    | 25,25' enriched electrolyte |
| 20 | 26     heater               |
|    | 27     pump                 |
| A  | anode                       |
| K  | cathode                     |